PREPARATION, CHARACTERIZATION AND ACTIVITY EVALUATION OF MULTI-COMPONENT PHOTOCATALYST UNDER VISIBLE LIGHT IRRADIATION

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ABSTRACT

The aim of the present work is to synthesize and characterize P-type, N-type and P-N type photocatalysts for wastewater treatment, to compare photocatalytic activity of different catalysts for dye degradation and to study the effect of visible light irradiation of difference parameter of photocatalytic reaction. Multicomponent P-type and P-N type photocatalyst were synthesized and characterized by XRD, SEM and BET. The visible light is used to study the catalyst activity for the composition of dye using photocatalyst. However, the photocatalytic activity under visible light is low. In order to increase its activity, multi-component photocatalyst is used. P-N-type semiconductor is used as the photocatalysts as it improve the photocatalytic activity using couple catalyst by accelerating the separation of electron-hole pair as well as to efficiently extend the region of visible light utilization. This research will demonstrated the feasibilities of the photocatalytic degradation of Methylene Blue for treating wastewaters where it is depends by varying the initial concentrations of Methylene Blue, addition amounts of P-type photocatalyst and the light irradiation. As a result, the photocatalytic activity followed the series of $CaFe_2O_4$-V_2O_5 >> $CaFe_2O_4$-WO_3 > $CaFe_2O_4$. Based on the findings of this study, some recommendation can be made which are calcinations of the catalyst with different temperature, effect of visible light power intensity and effect of different dopants and their characterization by XRD and XPS.

ABSTRAK

Matlamat projek ini adalah untuk mensintesis dan mengenalpasti pemangkin cahaya jenis P, jenis N dan jenis P-N untuk merawat sisa air, bagi membandingkan aktiviti pemangkin cahaya bagi setiap jenis pemangkin untuk degradasi pewarna dan bagi mengkaji kesan cahaya nampak ke atas perbezaan parameter untuk reaksi kepada pemangkin cahaya. Pemangkin jenis P dan pemangkin multi-komponen jenis P-N telah disintesis dan dikenalpasti oleh XRD, SEM dan BET. Cahaya nampak digunakan untuk mengkaji aktiviti pemangkin bagi komposisi pewarna menggunakan pemangkin cahaya. Walau bagaimanapun, aktiviti pemangkin di bawah cahaya nampak adalah rendah. Bagi menaikkan aktiviti cahaya nampak, pemangkin multi-komponen telah digunakan. Semi-konduktor jenis P-N digunakan sebagai pemangkin kerana ia meningkatkan aktiviti pemangkin cahaya dengan mempercepatkan pembahagian lubang elektron dan cekap memanjangkan rantau cahaya nampak. Kajian ini akan menunjukkan kesesuaian metilena biru bagi merawat sisa air, di mana ia bergantung kepada kepekatan awal metilena biru, berat pemangkin cahaya yang digunakan dan penyinaran cahaya nampak. Sebagai kesimpulannya, aktiviti pemangkon cahaya adalah mengikut siri $CaFe_2O_4$-V_2O_5 >> $CaFe_2O_4$-WO_3 > $CaFe_2O_4$. Berdasarkan kajian yang dijalankan, beberapa cadangan boleh dibuat dengan membakar pemangkin cahaya pada suhu yang berbeza, mengenalpasti kesan perubahan ke atas kuasa keamatan cahaya nampak dan mengenalpasti kesan ke atas jenis dopan yang berbeza dan ciri-cirinya dengan menggunakan XRD dan XPS.

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η	Photocatalytic efficiency
C_0	Concentration of reactant before illumination
C_t	Concentration of reactant after illumination time *t*
B	Crystallite size
K	Scherrer constant
λ	Wavelength
L	Line broadening at half maximum intensity (FWHM)
Θ	Peak position
q	Kinetic rate constant
q_α	Maximum adsorption capacity
K	Adsorption equilibrium constant
C	Volume of methylene blue
w	Weight of photocatalyst
k	Rate constant
t	Illumination time

LIST OF ABBREVIATIONS

CdS	Cadmium Sulfate
CdSe	Cadmium Selenide
UV	Ultra violet
XRD	X-Ray diffraction
BET	Brunauer-Emmett-Teller
SEM	Scanning Electron Microscopy
B	Boron
Si	Silicon
Sb	Antimony
$CaFe_2O_4$	Calcium Iron Oxide
$Ca(NO_3)_2 \cdot 4H_2O$	Calcium Nitrate
$Fe(NO_3)_3 \cdot 9H_2O$	Iron Nitrate
NH_3	Ammonia
WO_3	Tungsten Oxide
V_2O_5	Vanadium Pentoxide
$C_{16}H_{18}N_3SCl$	Methylene Blue

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Photocatalytic degradation of organic pollutants is one of the promising processes for environmental purification. The photocatalysis was revealed more than fifty years ago. Its use appeared in Japan in 1967, thanks to Professor Akira Fujishima. Researches and development continued and it was within the Japanese statecraft that the first realizations came out in 1990. The adventure of the photocatalysis can then expand rapidly in the European laboratories where it is set in numerous sectors and industrial applications: the building, the automobile or the household electrical appliances, the lighting and the sanitary (Carre, 2008).

Numerous studies have attempted to develop visible light driven photocatalysts in order to utilize solar energy and indoor light efficiently. There are two ways to exploit photocatalysts responsive to visible light irradiation (Tang *et al.*, 2004).

i. to generate intermediate energy levels in UV-active photocatalysts, such as TiO_2, by doping other elements to turn them into visible light photocatalysts
ii. to develop new materials with photocatalytic activity under visible light irradiation

Since few materials can provide both photo-oxidation power and photo-reduction power (which are necessary for complete decomposition of harmful organics) and, at the same time, can absorb visible light efficiently, composite photocatalysts with two or more components were extensively explored, and improved photocatalytic performance was obtained from various composite photocatalysts. (Liu, 2009)

Previous studies of visible light photocatalysts are using unstable upon illumination of light for example CdS and CdSe and low photocatalytic activity. Recently, some UV active oxides functioned as visible light photocatalysts by substitutional doping of metals but these doped materials only show small absorption on visible light region (Kim, 2005).

Multi-component photocatalyst or couple catalyst is one of the new techniques that is used to improve the photocatalytic activities by accelerating the separation of electron-hole pairs and to efficiently extend the region of visible light utilization. Technology has been discovered that the photocatalytic activity of multi-component photocatalyst is higher than that of the single one itself. This is because some of single photocatalyst should satisfy the stringent requirements of both band gap energy and band position. When the single photocatalyst cannot meet these requirements, using the multi-component photocatalyst should be an alternative. (Kim, 2005).

It is known that $CaFe_2O_4$ is p-type semiconductor; meanwhile WO_3 and V_2O_5 are n-type semiconductor. Theoretically, when p-type $CaFe_2O_4$ and WO_3 or V_2O_5 form p–n junction, the photogenerated electrons and holes are separated efficiently, and the photocatalytic activity is enhanced. In this study, p-type $CaFe_2O_4$ powder was prepared by precipitation method. In the presence work, characterization methods were employed are XRD, BET and SEM.

1.2 PROBLEM STATEMENT

The water quality nowadays has becoming environmental major concerns. The fact that using energy to eliminate such environmental contamination will result unstable environmental impact, however, leads us to a dilemma not to use energy to achieve our anti-pollution goal. Photocatalyst is a new material that can gently harmonize the contaminated environment to restore original conditions by using natural energy which is a part of the environment and low-cost energy supplied to our daily home life.

Mainly, photocatalytic is being done under ultra-violet (UV) light because it has more energy than visible light and mostly it generate suitable amount of energy for single photocatalyst to get excited. In this research, the visible light is use to treat the organic compound using photocatalytic. However, the photocatalytic activity under visible light is low. In order to increase its activity, multi-component photocatalyst is used.

1.3 RESEARCH OBJECTIVES

The objectives of this project are:

i. To synthesize and characterize P-type, N-type and P-N type photocatalysts for wastewater treatment

ii. To compare photocatalytic activity of different catalysts for dye degradation

iii. To study the effect of visible light irradiation of difference parameter of photocatalytic reaction.

1.4 RESEARCH QUESTIONS

i. What is the photocatalytic degradation efficiency of dye using P-N type photocatalyst?

iv. What is the comparison of the photocatalytic activity of different catalysts for dye degradation?

ii. What is the effect of visible light irradiation of difference parameter on photocatalytic reaction?

1.5 SCOPE OF STUDY

This research focuses on the synthesis P-type and P-N type photocatalyst for wastewater treatment under visible light irradiation by using precipitation method. The effect of visible light irradiation of difference parameter of photocatalytic reaction of this chosen system has also been studied and recorded. Methylene blue is used as the model substance.

The equipment that use in this experiment is Xenon Lamp and UV-Vis spectrophotometer.

1. In this research, the degradation process has been conducted at constant methylene blue concentration (50ppm). The catalyst amount is between 0.2-2.0 g.
2. The experiment carried out at two temperature condition which are T= (45 ± 5) °C and T= (30 ± 5) °C the irradiation process will be conducted from 0 min to 120 min.

Characterization of the catalysts was carried out using analytical instruments which include the X-Ray diffraction (XRD), Brunauer-Emmett-Teller (BET) and Scanning Electron Microscopy (SEM).

1.6 SIGNIFICANCE OF STUDY

With the significant increase in demand for water attention on reuse and recycling of wastewater has significantly increased. The method of photocatalytic degradation has many characteristics such as convenient safety, credibility and high efficiency. It helps to achieve standard pollution control and prevent environmental pollution**.** Thus, it is useful and advantageous to improve wastewater effluent. This technology can be commercialized for industrial application

1.7 DEFINITION KEY OF TERMS

i. Photocatalytic:

A process which a substance of photocatalyst introduces a chemical reaction under the action of the light, without undergoing any deterioration.

It is also a process by which free radicals are generated through the creation and subsequent separation of electron hole pairs formed in the presence of light, that are capable of breaking up complex organic molecules into smaller fragments

ii. Multi-component Photocatalyst:

A technique to improve the photocatalytic activity properties is by using couple catalyst where it used to accelerate the separation of electron-hole pair as well as to efficiently extend the region of visible light utilization.

iii. Visible Light :

Visible light is a range of electromagnetic radiation that can be detected by the human eye. The wavelengths associated with this range are 380 nm to 750 nm.

1.8 Conclusion

In conclusion, the method of photocatalytic degradation has many characteristics such as convenience, safety, credibility and high efficiency. So, it is hopeful that this method is extended and applied in the treatment of non-transparent or low-transparent wastewaters on the basic of more research work.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The Photocatalysis is a process in which a substance, the photocatalyst, introduces a chemical reaction under the action of the light, without undergoing any deterioration. It is also a process by which free radicals are generated through the creation and subsequent separation of electron hole pairs formed in the presence of light, that are capable of breaking up complex organic molecules into smaller fragments (Baruah, 2008). It used to degrade the material under the effect of the rays of light.

2.2 MULTI-COMPONENT PHOTOCATALYST

One technique to improve the photocatalytic activity properties is by using couple catalyst where it used to accelerate the separation of electron-hole pair as well as to efficiently extend the region of visible light utilization. This couple has been studied intensively by Chen Shifu *et al* and the result that the photocatalytic activity of couple catalyst is higher than that of the single one.

2.2.1 P-type Semiconductor

Generally, adding some percentage of foreign atoms in the regular crystal lattice will produce changes in its electrical properties for producing P-type and N-type semiconductor. This is also refers to the theory band of energy where extra levels have been added by the impurities for a certain energy to allow excitation of valance band electrons.

The P-type semiconductor can be defined as the addition of trivalent impurities to an intrinsic semiconductor that will create the deficiencies of valence electron, called "holes". The **Figure 2.1** shows the example of P-type semiconductor where Boron is added into Silicon material and create extra hole of energy level.

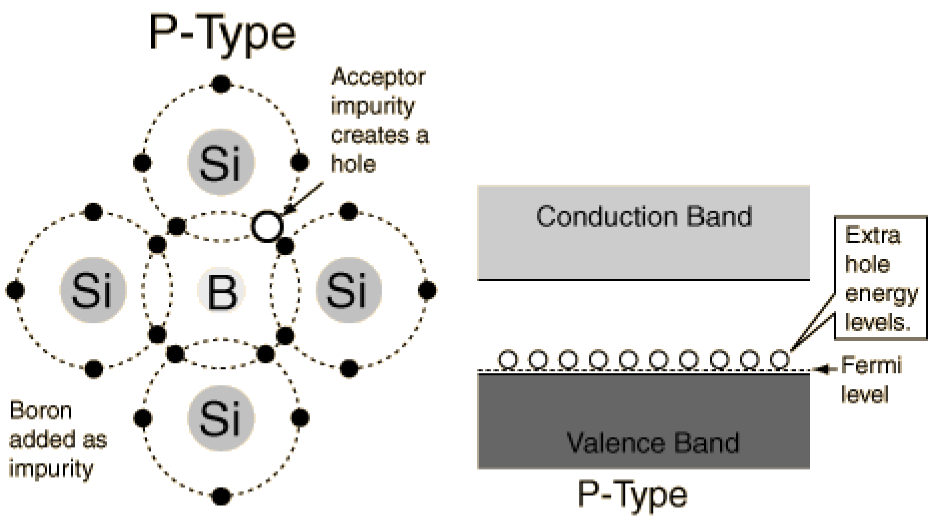

Figure 2.1: Example of P-type semiconductor

The addition of acceptor impurities contributes hole levels low in the semiconductor band gap so that electrons can be easily excited from the valence band into these levels, leaving mobile holes in the valence band. Electrons can be elevated from the valence band to the holes in the band gap with the energy provided by an applied voltage. Since electrons can be exchanged between the holes, the holes are said to be mobile. The holes are said to be the "majority carriers" for current flow in a P-type semiconductor. (Nave, 2005)

2.2.2 N-type Semiconductor

N-type semiconductor is produce as the impurities of 5 valance electron (pentavalent impurities) is being contributed by extra electrons. The contribution of free electrons wills greatly increasing the conductivity of intrinsic semiconductor.

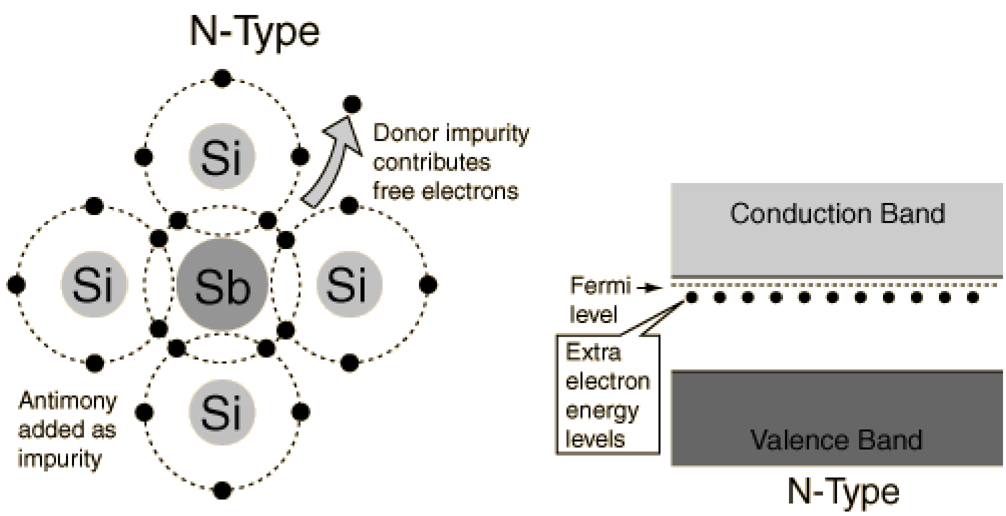

Figure 2.2: Example of N-type semiconductor

Referring to example of N-type semiconductor on **Figure 2.2,** the electrons can be elevated to the conduction band with the energy provided by an applied voltage and move through the material. The electrons are said to be the "majority carriers" for current flow in an N-type semiconductor (Nave, 2005).

2.2.1 P-N type Semiconductor

Photocatalyst should satisfy the stringent requirements of both gap energy and band positions. When the single component photocatalyst cannot meet these requirements, employment of multi-component photocatalyst should become an alternative. (Lee *et al.*, 2006)

There are 3 ways to combine the functions of different materials which are:

i. Simply mix an oxidation-type photocatalyst and reduction-type photocatalyst in a solution containing redox couple as electron shuttle
ii. Intercalate nano-particles of a photocatalyst into the layer of semiconductor
iii. Couple two semiconductors with different band position for efficient and longer charge separation

In photovoltaic cells that diode structure made of P-type and N-type semiconductor shows greatly enhanced activities compared to devices consisting of a single semiconductor (Khaselev, 1998). This formation of P-N type junction photocatalyst could lead to an efficient electron-hole separation that minimises the recombination of photo-excited electrons hole. (Jang *et al.*, 2007)

2.3 Reaction Mechanism

Photocatalytic activity mainly depends on whether the electron hole pairs can be separated effectively. Photocatalytic reaction is effective only when photo-excited electron holes can be captured or they will combine each other and give off heat on the surface of semiconductor. Refers to mechanism separation of electrons and holes, in order to increase photocatalytic activity two things must be considerate:

- To increase the separation efficiency of the photo-excited electron-hole pairs
- To increase the amount of photo-excited activity species

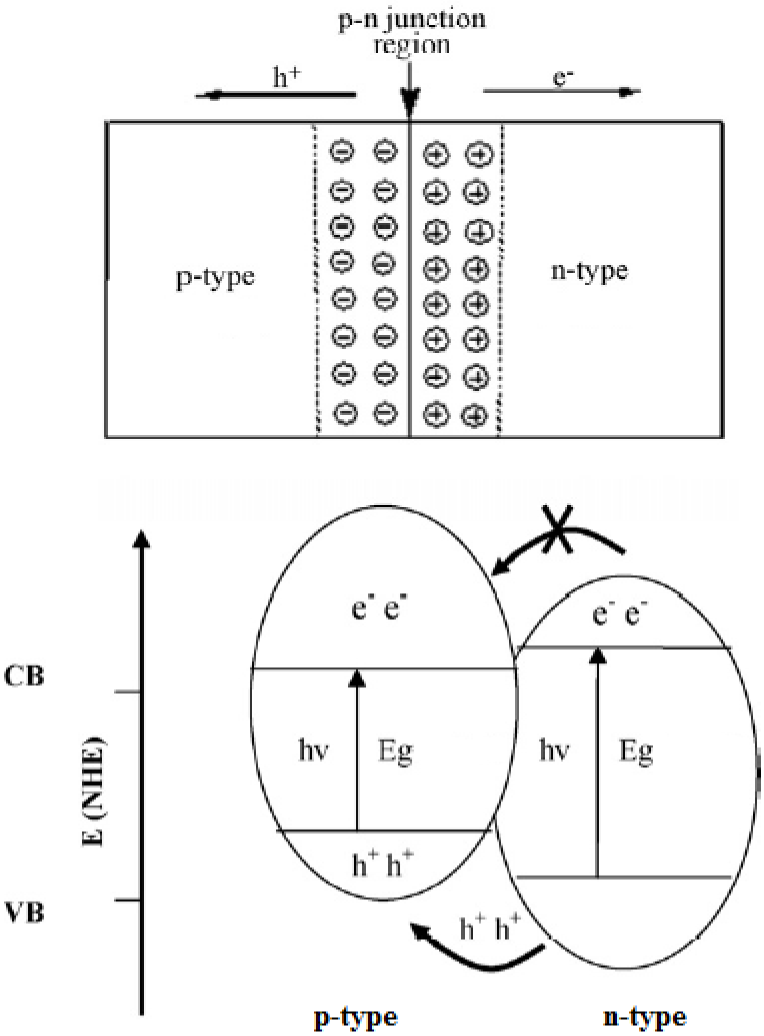

Figure 2.3: P-N junction formation model and schematic diagram of electron hole separation process

According to the position of band energy, the photo-excited holes can transfer from valence band of n-type to valance band of p-type but photo-excited electron cannot transfer from n-type to p-type because it will reduce the photocatalytic activity. The P-N junction formation model and schematic diagram of electron hole separation process is explained in **Figure 2.3**.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 THE SAMPLES MATERIALS

To provide the P-N junction photocatalyst in this research, the P-type semiconductor that will be used is Calcium Iron Oxide, $CaFe_2O_4$. Meanwhile N-type catalysts which are Tungsten Oxide, WO_3 and Vanadium Pentoxide, V_2O_5 will be mixed with $CaFe_2O_4$ to produce couple catalyst.

The materials that will be used to prepare the P-N junction photocatalyst are as in the **Table 3.1** follow.

Table 3.1: Experimental materials

Name	Structure	Purity
Calcium Nitrate	$Ca(NO_3)_2{\cdot}4H_2O$	99%
Iron Nitrate	$Fe(NO_3)_3{\cdot}9H_2O$	99%
Ammonia	NH_3	30%
Tungsten Oxide	WO_3	99%
Vanadium Pentoxide	V_2O_5	99%
Methylene Blue	$C_{16}H_{18}N_3SCl$	99%